

Morphologies of Polyethylene–Ethylene/Propylene/Diene Monomer Particles in Polypropylene-Rich Polyolefin Blends: Flake Structure

Todor Nedkov,¹ František Lednický²

¹*Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 103-A, BG-1113 Sofia, Bulgaria*

²*Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

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ABSTRACT: Morphologies of polyethylene–ethylene/propylene/diene monomer (PE/EPDM) particles in 93/7 polypropylene (PP)/PE blends were investigated. SEM micrographs of KMnO₄-etched cut surfaces and fracture surfaces of the blends revealed the existence of the “flake” structure. In the particles, crystalline PE formations with flake shape, which remain after etching, are called flakes. In addition to the PE-crystalline flakes, amorphous PE, located between PE crystalline lamellae and EPDM rubber, complement the flake structure. The flakes are usually linked with the PP matrix, as seen in the heptane-treated cut surfaces. These links, although observed with compatibilized sam-

ples, originate from the crystalline nature of PE particles, if no compatibilizer is added. Separately, the morphology of Royalene (consisting of high-density PE and EPDM rubber, used as a PP/PE compatibilizer) was investigated by low-voltage scanning TEM. The interaction of the components in the PE/EPDM blends can explain the formation of the flakes and toughening of the PP/PE blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3087–3092, 2003

Key words: blends; compatibilization; PE/EPDM blends; polyolefins; low-voltage scanning TEM

INTRODUCTION

Polypropylene (PP) and polyethylene (PE) are the most important representatives of polyolefins and are the major constituents of plastic waste and scrap. During collecting and sorting of the waste, PP and PE are usually considered as one group, if no special procedure such as magnetic separation systems (MSS), including infrared, X-ray, and color sensors, is used.¹ PP and PE are immiscible,² forming two phases when melted, and consequently the mechanical properties of their blends are unsatisfactory.

One way to improve toughness, which does not change chemical structure and does not produce crosslinking in the blend (i.e., allows reprocessing of the material more than once³) is the usage of compatibilizers.

Ethylene/propylene/diene monomer (EPDM) is a well-known impact modifier for PP^{4,5} and compatibilizer for PP/PE blends.^{6–8} It is known that the compatibilizer during blending is located at the interface between PE and PP phases. The interaction between

PE and EPDM rubber is important for the toughness of the PP/PE blend. Several kinds of PE/EPDM morphologies were previously published [Fig. 1(A)–(D)]: core–shell structure,^{9,10} interpenetrating phase structure,^{6,8,9} and incomplete core–shell structure.¹¹ Some links and protrusions between the PP matrix and PE/rubber particles were also reported.^{12,13} However, the complex supermolecular arrangement in the PE/EPDM part of compatibilized PP/PE blends and its role in imparting toughness to PP/PE blend are still not well understood.

The aim of this investigation was to elucidate the complex character of the textures in compatibilized PP/PE blends and PE/EPDM interaction.

EXPERIMENTAL

Materials

Blends of virgin material components and industrial recyclates were examined. The virgin materials were low-density polyethylene (LDPE) PFS 4020 and polypropylene (PP) R 401 received from Terplast (Poland). The compatibilizer Royalene IM 7565 was produced by Uniroyal Chemical Co. (Naugatuck, CT). The virgin materials are characterized in Table I.

Royalene IM 7565 is a blend of Royalene 580HT and high-density polyethylene (HDPE) (65 : 35). Royalene 580HT is an ethylene/propylene (E/P) copolymer

Correspondence to: T. Nedkov (tnedkov@moew.government.bg).

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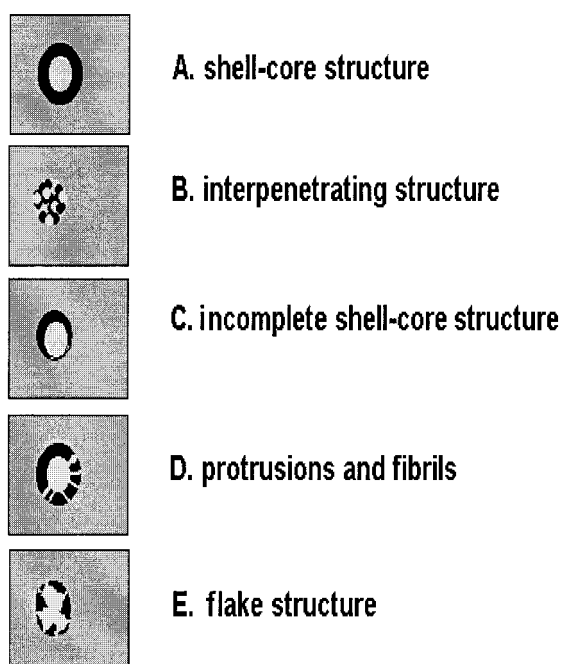


Figure 1 Representations of previously reported structures (A,^{9,10} B,^{6,8,9} C,¹¹ D^{12,13}) and of the flake structure (E). PE particle: light gray; PP matrix: dark gray; compatibilizer: black.

with an E/P ratio of 52/48 and its use is more suitable than use of the usual EPDM rubber. Industrial recycled materials are mixtures of the same types of PP and PE in the ratio 93/7, to which has been added 0.033% Irganox 1010, 0.067% Irgafos 168, and 0.1% calcium stearate. The recycled materials are scraps from the conveyor for preparing PP ropes. The PP/PE scraps were milled and then washed.

Blending and sample preparation

The model (virgin) and recycled samples were prepared from virgin and industrial material of PP/PE composition 93/7, to which 0, 1, 2.5, 5, and 10% Royalene was added. For mixing, a Brabender Plasticorder with W50EH chamber was used. The working volume of the mixing chamber was 50 cm³. Blends were mixed at 190°C for 10 min, at 60 rpm.

After mixing, the blends were removed from the mixing chamber and compression-molded in a Fontijne press at 3 MPa for 5 min at 200°C. The blends were prepared as 175-mm square plates with 1.3–1.5 mm thickness. Finally, the press was water-cooled to room temperature within about 10 min.

SEM

Cut surfaces were obtained with an ultramicrotome at –60°C (Ultratome III; LKB, Bromma, Sweden). The first set of the cut surfaces was etched in 2% solution of KMnO₄ in H₃PO₄ for 10 min, then washed with fresh permanganate solution and water. The second set of the cut surfaces was etched in heptane at room temperature, then washed with fresh heptane and water. The fracture surfaces were obtained from a notched impact fracture experiment at room temperature. Specimens were mounted on a SEM-holder and fixed with a silver paste. They were sputter-coated to obtain an approximately 4-nm-thick layer of platinum. SEM observations were performed on a JSM 6400 (JEOL, Tokyo) device. An accelerating voltage of 25 kV and a working distance of 8 mm were used.

Low-voltage scanning transmission electron microscopy (LV-STEM)

Low-temperature ultrathin sections of about 30 nm thick (specimen holder temperature –130°C, diamond knife temperature –60°C) were obtained with the ultramicrotome Leica Ultracut LCT with FC-S cryo-attachment. The LV-STEM observations were carried out on a VEGA TS5130 (Tescan, Brno, Czech Republic) device, in the bright-field mode, accelerating voltage of 15 kV, and 5.4 mm working distance.

RESULTS AND DISCUSSION

Practically speaking, there are no differences between the mechanical properties of virgin and recycled samples¹⁴ and the morphology of two sample sets is similar.

The particle morphology in compatibilized samples differs from that in the samples without compatibi-

TABLE I
Characteristics of the Virgin Materials: Number-Average Molecular Weight (M_n), Melt Flow Index (MFI), X-ray Degree of Crystallinity, and Glass-Transition Temperature (T_g)^a

Material	M_n	MFI (g/10 min)	Density (g/cm ³)	X-ray degree of crystallinity (%)	T_g (°C)
PP R 401	45,000	2.4–3.2	0.89	47.6	–10
PE PFS 420	40,000	1.8–2.6	0.92	33.5	–120
Royalene IM 7565	—	0.7–1.5	0.89	18.0	—

^a Data from manufacturers.

lizer. The main difference is the “flake” structure, represented schematically in Figure 1, where it is compared with other previously reported PE/EPDM particle morphologies in polyolefin blends. The location of compatibilizer at the interface defines the differences between the described structures as shown in Figure 1. A theoretical model at the molecular level of the flake structure and morphology of a particle are given in Figure 2. The model is based on the experimental results (Figs. 3–6).

Micrographs, on the basis of which the flake structure is proposed [Fig. 3(a)–(c)], show a cross section of the bulk of investigated blends after cutting with a glass knife at -60°C and subsequent permanganate etching. Permanganate etching is known to attack and remove the accessible amorphous part of PE and PP, whereas the crystalline parts of polyolefins are much more stable to the etching agent.¹⁵ The flake structure is composed of the crystalline PE part, which remains after permanganate etching. If this flake structure is conceivably complemented to the spherical/cylindrical shape of particles with Royalene and amorphous PE, we should obtain the structure that exhibits intrinsic flake features, as well. In fact, this structure is really present in the blends if no permanganate etching is used.

The flake structure is intermediate between core-shell and interpenetrating phase structures (cf. Fig. 1), which are obtained at very low and very high cooling rates of the melt, respectively.⁶ The flake structure appears to be obtained at intermediate cooling rates. Although probably often formed, the flake structure has not yet been described in the literature, given that significant microscopic work was needed for its identification.

The theoretical model presents the particle morphology and interface between the PP matrix and PE particles in the case of a noncompatibilized blend [Fig. 2(a)] and between the PP matrix and PE/rubber particles in the case of a compatibilized blend [Fig. 2(b)].

The model implies that PE and rubber are partly miscible, whereas PP is assumed immiscible with PE and with rubber. However, some PE crystalline lamellae, which form the ends (edges) of flakes, penetrate through the matrix–particle border into the PP matrix: protrusions [Fig. 4(a), (b)] and links [Figs. 4(c), 5] constitute the evidence for this penetration. In the case of noncompatibilized samples [Fig. 4(a), (b)], protrusions rather than links are typical.

Particle dimensions vary between about 0.1 and 1 μm . Their corresponding volume is usually insufficient for producing PE spherulites or other higher-ordered crystalline structures (i.e., axialites or dendrites), and such formations are not observed in the cut particles. However, WAXS results¹⁴ show that PE exists in the crystalline state in the blends and imply the presence of some stacks of lamellae, which can be

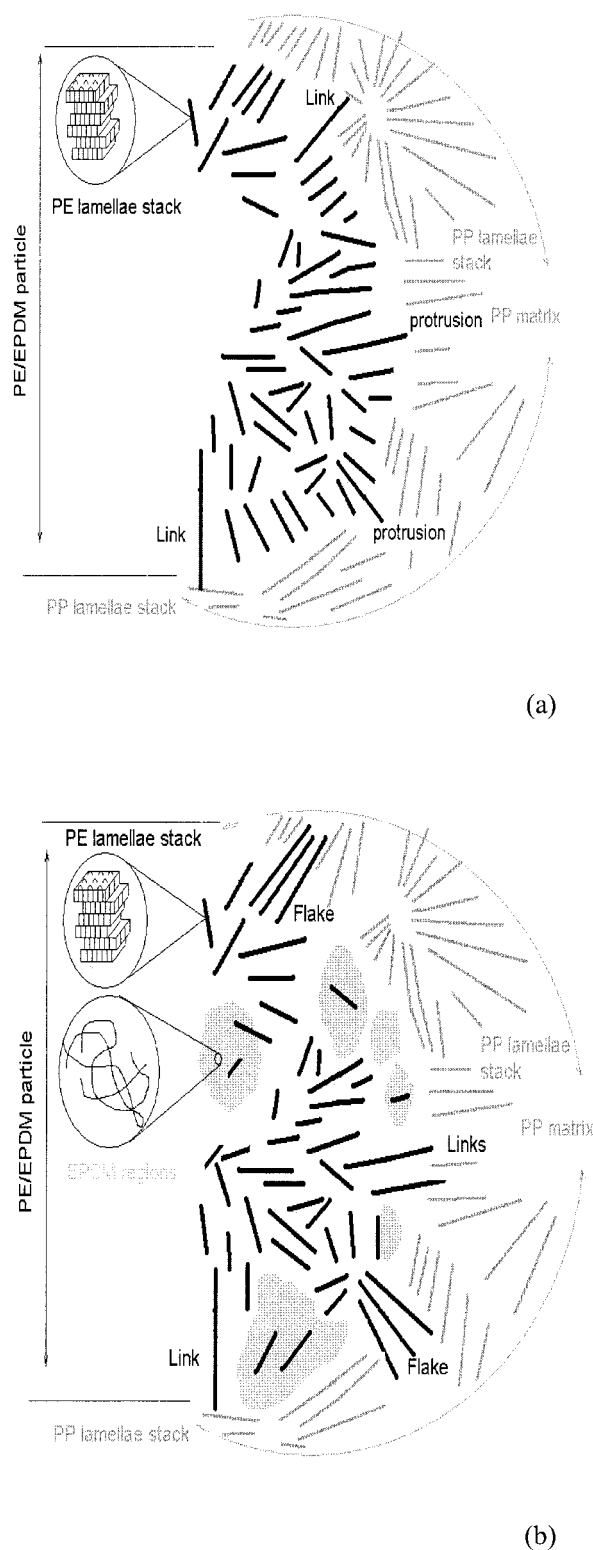


Figure 2 Interaction between matrix and particle: (a) noncompatibilized sample; (b) sample compatibilized with 10% Royalene. For clarity, only half of the particle is presented.

observed in PE particles [Fig. 4(a)]. These lamella stacks appear as small white spots in the particle on the right-hand side of the micrograph. Figure 4(b)

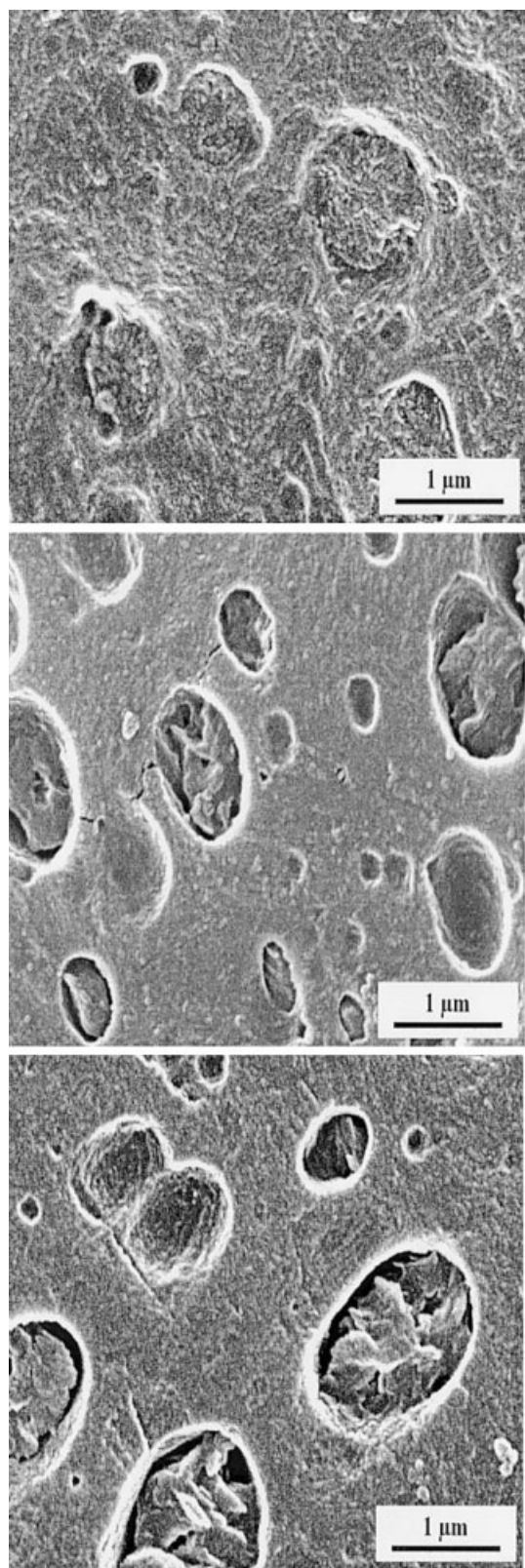


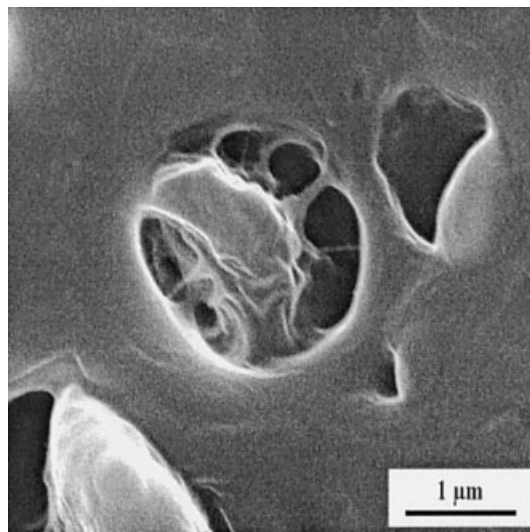
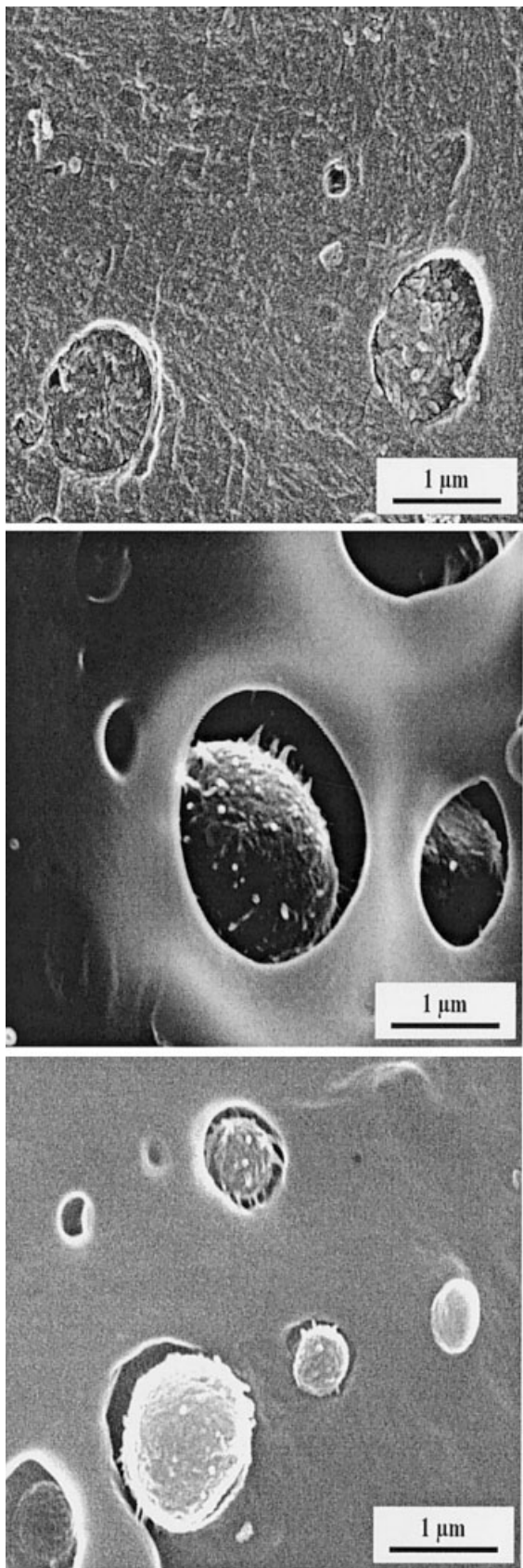
Figure 3 Flake structure: (a) noncompatibilized sample; (b) sample with 5% Royalene; (c) sample with 10% Royalene. Virgin samples; cut surfaces, permanganate etching. Length of images: 4.7 μm .

presents the fracture surface of the examined noncompatibilized blend. Some small white points (top view) or protrusions (side view) can be observed on PE particles [Fig. 4(a), (b)]. In some cases, they jut out from the particles [Fig. 4(b)] and are even connected with the matrix [Fig. 4(c)]. These protrusions should correspond to the crystalline lamella stacks, which are possibly drawn and can be observed on the etched cut surfaces [Fig. 4(a)]. Comparing cutting and fracture, it should be taken into account that cut surfaces are obtained at -60°C , whereas fracture surfaces are obtained at room temperature. The temperature difference between two preparation techniques is even higher than 80°C because of local overheating occurring during the fracture process.¹⁶ The increased temperature can explain the conversion of crystalline lamella stacks into the observed protrusions.

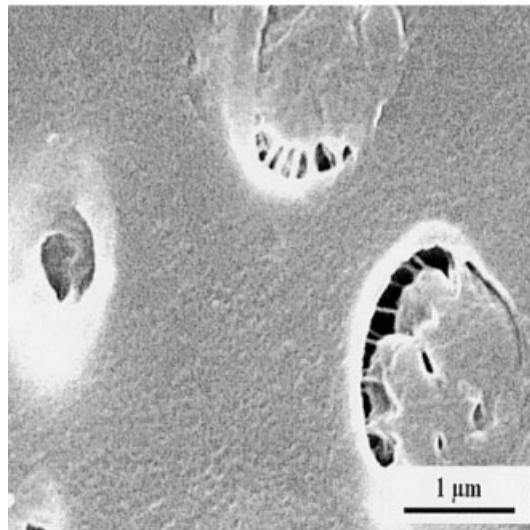
(a) In the case of compatibilized samples [Fig. 5(a), (b)], links or bridges are typical. The crystalline protrusions, which are observed in the noncompatibilized sample in the micrographs of fracture surface [Fig. 4(b), (c)], are replaced by links or bridges in compatibilized samples [Fig. 5(a), (b)]. With compatibilized samples (fracture surfaces), the particles seem to be composed of textures like terraces, which resemble the flake structure observed on cut surfaces. They seem to be enveloped by a deformed layer, a part of which remains connected to the matrix [Fig. 5(a)]. In this micrograph, bridges or links between particles and matrix remaining from the wrapping layer are thicker and evidently tougher than those obtained in noncompatibilized blends, in the few places where they appear.

(b) Figure 5(b) presents cut surfaces of samples compatibilized with 10% Royalene, etched in heptane. Whereas the solution of KMnO_4 in H_3PO_4 corrodes both the amorphous part of polyolefins and the EPDM rubber as well, heptane extracts only the rubber from the blend. Consequently, inclusions, but not holes, can be seen in the micrographs of specimens etched in heptane. These micrographs show that the compatibilizer is not incorporated separately in the matrix but is located around PE particles. In some particles [Fig. 5(b)], the same flake structure, as in the samples etched with KMnO_4 , can be observed. The etching in heptane better reveals the existing bridges or links between particles and matrix. These connections cannot be rubber because the EPDM rubber part from Royalene would be dissolved in heptane. It is not possible to distinguish whether they come from the HDPE part of Royalene or whether they originate from the 7% of the original LDPE in the blend.

The structure of Royalene blend is presented in Figure 6. The HDPE part of Royalene constitutes 35% and the EPDM rubber 65% of Royalene. According to the composition, the matrix in the micrograph, which appears white, should be the rubber, whereas the



(a)



(b)

(a)

(b)

Figure 5 Compatibilized sample with 10% Royalene: (a) fracture surface, virgin sample; (b) cut surface, solution in heptane, recycled sample. Length of images: 4.7 μm .

black spots should consist of HDPE. The evidence is also corroborated by the densities of both components. HDPE's density is 0.96 g/cm^3 , whereas that of EPDM is 0.85 g/cm^3 (Royalene 0.89 g/cm^3). As the LV-STEM is used, the blend is not stained, and the darker structure represents the higher-density component, the HDPE. The interaction between HDPE and EPDM rubber is complex. Both phases have no clear borders and merge one into another. The structure appears in the border between the two phases and in HDPE particles as well. The structure is finer inside the particles. As is clear from the WAXS pattern of the com-

(c)

Figure 4 Noncompatibilized samples: (a) cut surface, permanganate etching, recycled sample; (b) fracture surfaces, virgin sample; (c) fracture surfaces, recycled sample. Length of images: 4.7 μm .

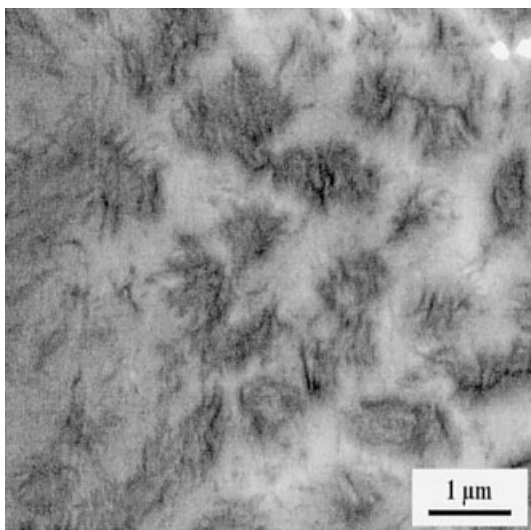


Figure 6 Structure of Royalene by LV-STEM (ultrathin section).

patibilizer, the HDPE part of Royalene crystallizes; thus the observed structure can be crystalline lamellae or stacks of lamellae. It is more probable that this structure is composed of lamellae stacks, given that the "long period" of Royalene is 255 Å,¹⁴ whereas the measured repeated distance between "bones" varies between 600 and 1000 Å. The structure of Royalene (Fig. 6) shows the strong interaction between PE and EPDM and implies the formation of flake structure in the course of the blending process.

CONCLUSIONS

A new arrangement in dispersed PE/rubber particles in the PP matrix was described as a flake structure. The flake structure is composed of the crystalline PE part, which remains after permanganate etching, and appears to be intermediate between the core-shell and interpenetrating phase structures.

Some PE crystalline lamellae, which form the end (edge) of flakes, penetrate through the matrix-particle border into the PP matrix.

The morphology of Royalene demonstrates the strong and complex interaction between PE and EPDM and implies the formation of the flake structure in the course of the blending process.

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References

1. Kenny, G. R.; Morgan, D. R.; Stephens, A. H. *Proc Natl Waste Process Conf* 1992, 15, 307.
2. Wignall, G. D.; Child, H. R.; Samuels, R. J. *Polymer* 1982, 23, 957.
3. La Mantia, F. P. In: *Polypropylene*; Karger-Kocsis, J., Ed.; Kluwer Academic: Dordrecht, 1999; p. 702.
4. Lopez-Manchado, M.; Biagiotti, J.; Arroyo, M.; Kenny, M. J. *Macromol Symp* 1999, 148, 345.
5. Wal, A.; Mulder, J.; Oderkerk, J.; Gaymans, R. *Polymer* 1998, 39, 6781.
6. Ho, W.; Salovey, R. *Polym Eng Sci* 1981, 21, 839.
7. Kesary, J.; Salovey, R. In: *Polymer Blends and Composites in Multiphase System*, Han, C. D., Ed.; ACS Advanced Chemical Series 206; American Chemical Society: Washington, DC, 1984; p. 211.
8. Holtz, N.; Goizueta, G. S.; Capiati, N. J. *Polym Eng Sci* 1996, 36, 2765.
9. Stehling, F.; Huff, T.; Speed, C.; Wissler, G. *J Appl Polym Sci* 1981, 26, 2693.
10. Zheng, W.; Leng, Y.; Zhu, X. *Plast Rubber Compos Proc Appl* 1996, 25, 490.
11. Flaris, V.; Stachurski, Z. H. *J Appl Polym Sci* 1992, 45, 1789.
12. D'Orazio, L.; Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Silvestre, C. *Polym Eng Sci* 1982, 22, 536.
13. Petrovic, Z. S.; Budinski-Simendic, J.; Divjakovic, V.; Skrbic, Z. *J Appl Polym Sci* 1996, 59, 301.
14. Nedkov, T. *J Appl Polym Sci*, submitted.
15. Olley, R. H.; Basset, D. C.; Blundell, D. J. *Polymer* 1986, 27, 344.
16. Swallowe, G. M. In: *Mechanical Properties and Testing of Polymers*; Swallowe, G. M., Ed.; Kluwer Academic: Dordrecht, 1999; p. 216.